New Ultra Low Migration Solventfree Laminating Adhesive for Food Packaging

Randy A. Johnson, Ph.D.
and Lubica Alabakovska

Ashland Specialty Ingredients, Adhesives
Dublin, Ohio
ashland.com/safepackaging
+1 877 546 2782

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Flexible packaging laminating adhesives are used to bond two or more films, paper or foil together to protect the graphics of the package and/or add utility to the package. For example, a stand up food pouch may consist of reverse printed polyester film (PET) adhesively bonded to polyethylene film (PE). The PET film provides high gloss and scuff resistance to protect the printed graphics, while the PE film provides a surface that can be heatsealed to form a food containing pouch or bag. The adhesive must have good adhesion to the films and ink, good appearance, coat at high line speed without misting, good heat resistance, low / no migration into the packaged food, does not scavenge slip from the film and have good resistance to the ingredients being packaged.

Aromatic solventfree adhesives, otherwise known as 100% reactive, are an excellent choice for laminating adhesives. Typical features and properties of solventfree adhesives include:

- Two-components
  1. Polyisocyanate (usually MDI-based)
  2. Curative (mixture of polyols)
- Low initial mixed viscosity (1,000 – 3,000 cps); reaction begins immediately after mixing the two components
- Slightly over-indexed with isocyanate
- Low-to-zero green bond off-line; requires high tension control coater
- Cure rate is typically 1-3 days for general purpose and 7-14 days for applications requiring ultra low migration for food compliancy.

Two-component aromatic solventfree adhesives have been commercially successful due to the following advantages:

1. Versatility in formulating polyurethanes to meet adhesive performance requirements such as bond strengths, heat seal strength and product resistance.
2. Smaller capital investment for converters (i.e., lower cost equipment, no oven, no incinerator)
3. Less energy consumption due to no ovens or incinerator
4. Lower adhesive coat weight compared to solvent and water-based adhesives
5. Higher production line speeds
6. Low / no VOCs
7. Smaller floor space requirement

However, aromatic solventfree laminating adhesives do have disadvantages or limitations. Here are a few which inhibit the broader success of this technology:

1. Low-to-zero green bond; unable to laminate and slit in-line
2. Poor adhesion with some laminations using water-based inks
3. Barrier-to-barrier laminates (i.e., PET film to foil) made at high line speeds typically have trapped air bubbles.
4. Ultra low migration of aromatic isocyante in all food types (i.e., fatty, aqueuos, alcohol, and dry foods) which is increased in elevated temperature applications. Due to migration concerns, adhesives typically require many days to cure to meet FDA compliancy.

Solvent-based laminating adhesives and aliphatic solventfree urethane adhesives are typically used instead of aromatic solventfree urethane adhesives in medium-to-high performance applications such as cook-in-bag, microwavable and retort applications due to migration requirements. Current commercial aromatic urethane laminating adhesives can meet the higher performance requirements, but typically do not meet "fit for use" suitability for fatty foods at higher temperatures because of the migration of adhesive components. Aromatic solventfree adhesives are mostly used in low-to-medium demanding applications.

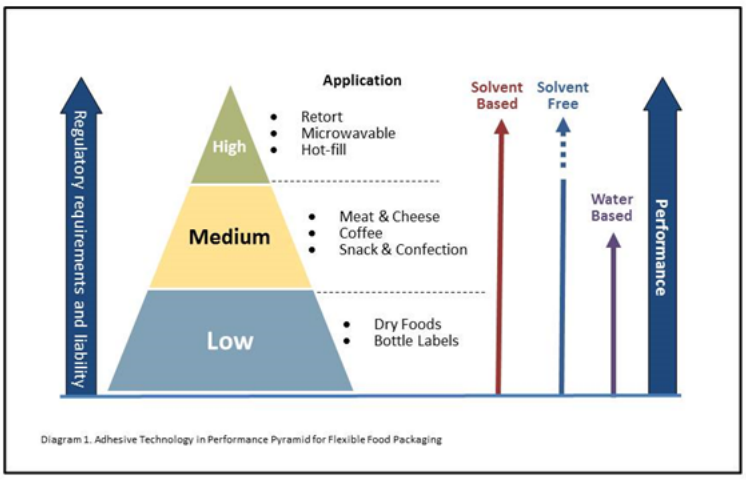

Diagram 1. Adhesive Technology in Performance Pyramid for Flexible Food Packaging

Market Opportunity

Through converter interviews, we were able to uncover the unmet need for a cost competitive, aromatic solventfree adhesive with all of the following benefits:

1. Ultra Low Migration – "fit for use" suitable for packaging of all food types (i.e., fatty, aqueuos, alcohol, and dry foods) and higher temperature applications.
2. Excellent bonds to clear and metallized films
3. Line speed > 1,300 fpm without misting
4. Fast curing – slit or run second pass lamination within hours

"Fit for Use" Suitability in Food Packaging

In the United States, suitability for use of adhesives in food packaging is based on risk. Risk is the result of the hazard associated with a specific migrant and exposure to the specific migrant.

Risk = Hazard x Exposure

Chemicals with lower hazards may be generally recognized as safe (GRAS) by the FDA or have higher migration limits compared to chemicals of higher hazards. Resin suppliers should have awareness of migrating components and understand the toxicology of each migrant.

Using this risk model, we developed a detectional limit for methylene diphenyl diisocyanate (MDI)/ methylene dianiline (MDA) based on 4,4'-methylene dianiline (a carinogenic by-product known to migrate from certain aromatic isocyanate-based adheisves). Using the hazard information for 4,4'-methylenedianiline and FDA's consumption factor (CF) of 5%, we identified an acceptable detection limit of 0.6 ppb for MDI/MDA.

Migration testing can be impacted by variables such as adhesive composition, cure time, sealant film and test conditions. Migration testing should be representative of the flexible food packaging application, end use conditions, and follow regional requirements (i.e., FDA). This article is only including regional requirements for FDA.

US FDA food simulants for migration testing (described in FDA's Guidance for Industry: Preparation of Premarket Submissions for Food Contact Substances: Chemistry Recommendations)

- Fatty foods 95% ethanol / 5% water
- Liquid foods 10% ethanol / 90% water
- Migration cells 10 mL of simulant / 1 in2 of film run in triplicate

Time and Temperature

- 70°C for 2 hours covers hot-fill (only)
- 40oC for 10 days migration covers one year shelf life (only)
- 70°C for 2 hours followed by 40°C for 10 days covers hot-fill and one year shelf life
- 121°C for 2 hours followed by 40°C for 10 days covers retort and one year shelf life

As described above, there are many things to consider when evaluating an adhesive's suitability for use in flexible food packaging.

The purpose of this article is to share our analyses of these options and identify a way to meet food packaging "fit for use" suitability through ultra low migration of a solventfree laminating adhesive. Our efforts in this work are focused on suitability for use in food packaging for North America (FDA). The adhesive technology may translate globally, but migration testing and suitability for food packaging use must be completed per regional requirements.

New Adhesive Technology

We developed a new two component urethane solventfree laminating adhesive with the following benefits:

1. Ultra Low Migration – suitable for all food types (i.e., fatty, aqueuos, alcohol, and dry foods)
2. Excellent bonds to clear and metallized films
3. Line speed > 1,200 fpm without misting
4. Fast curing – slit or run second pass lamination within hours

Due to our fomula being proprietary, we are only disclosing the component (MDI). This is the highest hazard ingredient and poses the most risk since MDI migrating into food can form derivatives which may include (MDA). Therefore, it will demonstrate best how to meet suitability for use in food packaging.

The new adhesive has a pot-life of 25+ minutes based on mixed adhesive viscosity < 5,000 cps at 35oC. Thus, allowing line operators time to shut down the equipment for various reasons. The adhesive also runs on smooth roll transfer at line speed > 1,200 fpm without misting.

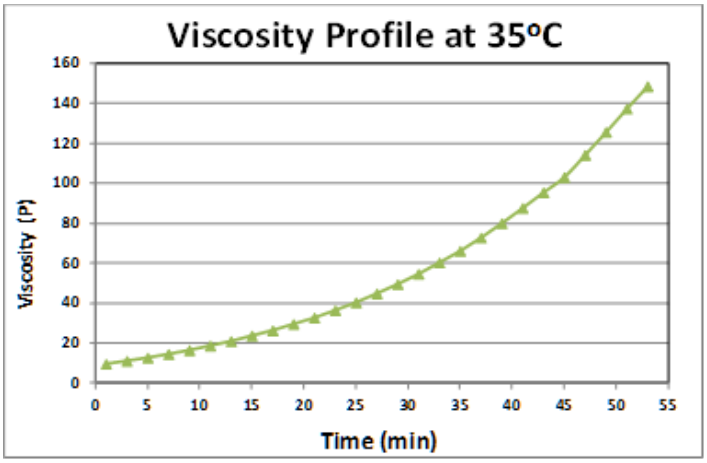

Diagram 2. Mixed Adhesive Viscosity Profile vs Temperature

The adhesive has very good appearance, excellent bond strength development (Diagram 3) and resistance to degrading from aggressive ingredients (Table 1).

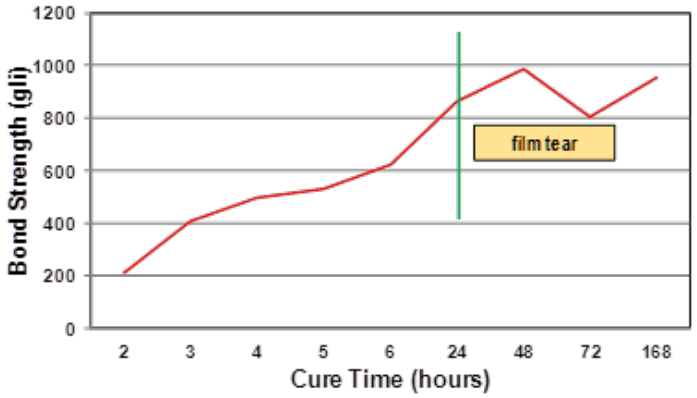

Diagram 3. New Adhesive Bond Strength Development; 48g PET / 1.5 mil LLDPE

Aggressive Ingredient	Laminations PET/PE
3% Acetic Acid	pass
BBQ Sauce	pass
Chocolate Syrup	pass
Coffee	pass
Conditioner	pass
Dog Food-Dry	pass
French Dressing	pass
Ground Cinnamon	pass
Gummy Bears	pass
Hazelnut Coffee	pass

Aggressive Ingredient	Laminations PET/PE
Iodine Swab	pass
IPA	pass
Ketchup	pass
Mineral Oil	pass
Rice	pass
Shampoo/Conditioner	pass
Sweet-Sour Sauce	pass
Tomato Sauce	pass
Vegetable Oil	pass

Table 1. Resistance to Aggressive Ingredients in PET / PE pouches at 60oC for 100hours.

Migration Results

Proprietary work methods were developed for the migration extraction solutions followed by liquid chromotography / mass spectrometry (LC-MS) analysis with LOD < 0.6 ppb.

Migration Testing Process (Key Steps):

1. Lamination - target 1.0 lb / ream of adhesive run on production coater at 1,200 fpm.
2. Adhesive cure time – variable
3. Migration cells – 10mL of simulant / 1 in2 lamination run in triplicate (FDA specificiation). See Diagram 4.
4. Migration time & temperature – variable
5. Analysis of migrants via triple quad liquid chromotography / mass spectrometry (LC/MS)

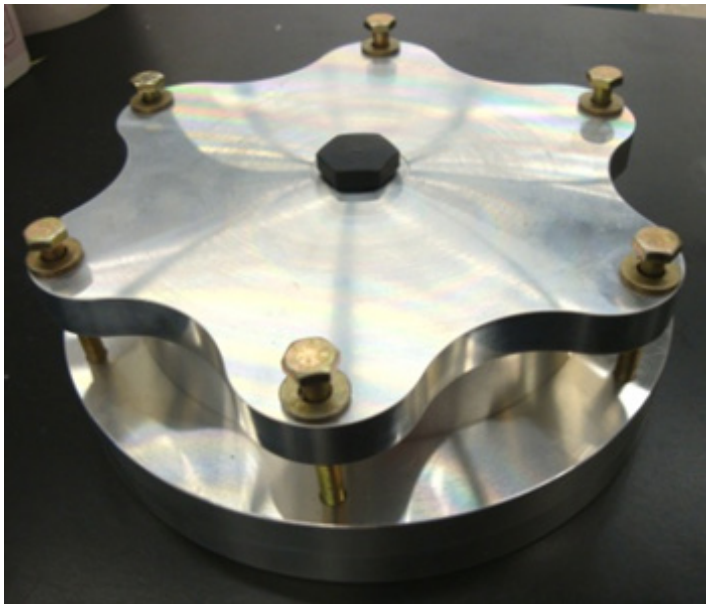

Diagram 4. Migration test cell (10 mL of simulant / 1 in2 of film)

Migration Constants:

- Adhesive composition – optimized initially for ultra low migration
- Coat weight – target 1.0 lb / ream
- Cure temperature – ambient temperature

Migration Variables:

- Adhesive cure time (days)
- Sealant film – type, thickness
  - LLDPE (3 mil)
- Food simulants
  - Fatty - 95% ethanol / 5% water
  - Aqueous - 10% ethanol / 90% water
- Time and temperature
  - 70°C for 2 hours
  - 70°C for 2 hours + 40oC for 10 days
  - 100°C for 2 hours + 40°C for 10 days

Table 2 has results of this new adhesive off of Ashland's production coater and for the most challenging food simulant of 95% ethanol. The results are extremely good with migration < 0.6 ppb within 3 days providing food packaging suitability for fatty foods used in conditions up to 100°C. Our presentation will include additional migration results for various sealant film thicknesses and compositions.

Adhesive:	**New Aromatic Urethane Solventfree Adhesive**		
Sealant film ID:	**3 mil LLDPE**		
Food Simulant:	**95% ethanol/ 5% water**		
Extraction:	**2h/100°C + 10 days/40°C**		
	Total MDI-DEU (ppb)		
Cure time	**Sample 1**	**Sample 2**	**Sample 3**
2 days	ND	ND	0.83
3 days	ND	ND	ND
4 days	ND	ND	ND
ND - not detectable at equivalent of 0.6 ppb MDI / MDA			

Table 2. Migration Results for New Adhesive

SUMMARY

The technology development of ultra low migration for aromatic urethane solventfree laminating adhesives for all types of foods in both clear and metallized flexible packaging was successful. Besides ultra low migration adhesives, "fit for use" suitability can also be met by selection of higher barrier sealant films, limiting end use application by market size or to less challenging applications. The challenge to prove up ultra low migration adhesives is being met with ultra high pressure liquid chromotography / mass spectrometry for identifying migrants to four decimal points in mass along with sub part per billion analysis.

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1 The consumption factor is a measurement of exposure. FDA defines the consumption factor (CF) as the fraction of a person's diet likely to include food-contact articles containing the chemical migrant. The use of a 5% CF was supported by an analysis market and packaging use data.

Global Headquarters
Ashland Inc.
50 East RiverCenter Blvd.
Covington, KY 41012 USA
Tel: +1 859 815 3333

Ashland Specialty Ingredients
8145 Blazer Drive
Wilmington, DE 19808 USA
Tel: +1 877 546 2782

Regional Centers
North America
Dublin, OH USA
Tel: +1 866 514 8898
adhesivesNA@ashland.com

Latin America
São Paulo, Brazil
Tel: +55 11 3649 0455
Fax: +55 11 3649 0450
Mexico City, Mexico
Tel: +52 55 5276 6110
Fax: +52 55 2614 2939

Asia Pacific
Singapore
Tel: +65 6775 5366
Fax: +65-6776 9690
Mumbai, India
Tel: +91 22 61484646
Fax: +91 22 61484639
Shanghai, P.R. China
Tel: +86 21 2402 4888
Fax: +86 21 2402 4850
adhesivesAP@ashland.com

Europe
Schaffhausen, Switzerland
Tel: +44 1562 821 207
adhesivesEMEA@ashland.com

Middle East and Africa
Dubai, U.A.E.
Tel: +971 4 381 8515
adhesivesEMEA@ashland.com

ashland.com

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